

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US2005/028637

International filing date: 11 August 2005 (11.08.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/602,183
Filing date: 16 August 2004 (16.08.2004)

Date of receipt at the International Bureau: 03 October 2006 (03.10.2006)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

September 22, 2006

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/602,183

FILING DATE: *August 16, 2004*

RELATED PCT APPLICATION NUMBER: PCT/US05/28637

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US60/602,183*



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

081604

17589 U.S. PTO

PTO/SB/16 (04-04)

Approved for use through 07/31/2006. OMB 0651-0032
 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

22264 U.S. PTO
 60/602183

081604

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
James T.		Leach		Dana Point, California	
Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number:		2675			
OR					
<input type="checkbox"/> Firm or Individual Name		Mr. William W. Haeffliger			
Address		201 S. Lake Ave., Suite 512			
Address					
City		Pasadena	State	CA	Zip
Country		USA	Telephone	323 684-2707	Fax
				91101	626 449-0520
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages		31		<input type="checkbox"/> CD(s), Number _____	
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets		2		<input type="checkbox"/> Other (specify) _____	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE Amount (\$)	
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees.				80.00	
<input type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: _____					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

[Page 1 of 2]

Respectfully submitted,

SIGNATURE

Date Aug. 13, 2004

TYPED or PRINTED NAME

William W. Haeffliger

REGISTRATION NO. 17,120

(if appropriate)

Docket Number: 12,641

TELEPHONE

322 684-2707

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

081604

17589

U.S. PTO

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Approved for use through 07/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 120.

Complete if Known

Application Number
Filing Date
First Named Inventor **James T. Leach**
Examiner Name
Art Unit
Attorney Docket No. **12,641**

METHOD OF PAYMENT (check all that apply)☒ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None☐ Deposit Account:Deposit Account Number
Deposit Account Name

08-0118

William W. Haefliger

The Director is authorized to: (check all that apply)

☐ Charge fee(s) indicated below ☐ Credit any overpayments☒ Charge any additional fee(s) or any underpayment of fee(s)☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.**FEE CALCULATION****1. BASIC FILING FEE**

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1001 770	2001 385	Utility filing fee	
1002 340	2002 170	Design filing fee	
1003 530	2003 265	Plant filing fee	
1004 770	2004 385	Reissue filing fee	
1005 160	2005 80	Provisional filing fee	80.
SUBTOTAL (1)			(\$) 80.

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims Extra Claims Fee from below Fee Paid
Independent Claims - 20** = X =
Multiple Dependent Claims - 3** = X =

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description
1202 18	2202 9	Claims in excess of 20
1201 86	2201 43	Independent claims in excess of 3
1203 290	2203 145	Multiple dependent claim, if not paid
1204 86	2204 43	** Reissue independent claims over original patent
1205 18	2205 9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2)

(\$)

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity Small Entity

Fee Code (\$)	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
1051 130	2051 65		Surcharge - late filing fee or oath	
1052 50	2052 25		Surcharge - late provisional filing fee or cover sheet	
1053 130	1053 130		Non-English specification	
1812 2,520	1812 2,520		For filing a request for ex parte reexamination	
1804 920*	1804 920*		Requesting publication of SIR prior to Examiner action	
1805 1,840*	1805 1,840*		Requesting publication of SIR after Examiner action	
1251 110	2251 55		Extension for reply within first month	
1252 420	2252 210		Extension for reply within second month	
1253 950	2253 475		Extension for reply within third month	
1254 1,480	2254 740		Extension for reply within fourth month	
1255 2,010	2255 1,005		Extension for reply within fifth month	
1401 330	2401 165		Notice of Appeal	
1402 330	2402 165		Filing a brief in support of an appeal	
1403 290	2403 145		Request for oral hearing	
1451 1,510	1451 1,510		Petition to institute a public use proceeding	
1452 110	2452 55		Petition to revive - unavoidable	
1453 1,330	2453 665		Petition to revive - unintentional	
1501 1,330	2501 665		Utility issue fee (or reissue)	
1502 480	2502 240		Design issue fee	
1503 640	2503 320		Plant issue fee	
1460 130	1460 130		Petitions to the Commissioner	
1807 50	1807 50		Processing fee under 37 CFR 1.17(q)	
1806 180	1806 180		Submission of Information Disclosure Stmt	
8021 40	8021 40		Recording each patent assignment per property (times number of properties)	40.
1809 770	2809 385		Filing a submission after final rejection (37 CFR 1.129(a))	
1810 770	2810 385		For each additional invention to be examined (37 CFR 1.129(b))	
1801 770	2801 385		Request for Continued Examination (RCE)	
1802 900	1802 900		Request for expedited examination of a design application	

Other fee (specify)

*Reduced by Basic Filing Fee Paid

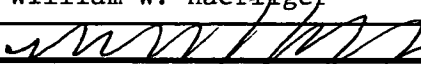
SUBTOTAL (3)

(\$)

40.

SUBMITTED BY

(Complete if applicable)

Name (Print/Type) **William W. Haefliger** Registration No. **17,120** Telephone **323 684-2707**
Signature  Date **Aug. 13, 2004**

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

CONTROLLED SPECTRUM ULTRAVIOLET RADIATION
NO_x REDUCTION PROCESS

FIELD OF THE INVENTION

5

10

15

20

This invention relates generally to reduction or elimination of oxides of nitrogen, ammonia, and carbon monoxide from hot gases, such as are produced from combustion processes, and it further relates to the use of ultraviolet radiation for reducing the concentration of such gases in or from effluent gas streams. More particularly, the present invention relates to a process for the photo-catalytic oxidation of ammonia (NH₃) and photo-catalytic reduction of nitrogen oxides, NO_x, (NO, N₂O, NO₂) to nitrogen gas (N₂) and water vapor (H₂O) at a low temperature range (100-400F). A secondary benefit is the photolysis of water vapor used to complete the oxidation of CO to CO₂ in the gas stream.

BACKGROUND OF THE INVENTION

25

Currently there are several techniques in use for reducing the amount of oxides of nitrogen (NO_x) released into the air from effluent exhaust gas streams. These are principally classified as techniques that are

applied at the origin of these gases, such as improving the control of combustion processes of hydrocarbon fuels and air, and processes that are applied to the gases after the NOx has been formed. Techniques that improve the control of the combustion process focus on the elimination of peak flame temperatures that are the primarily cause for the formation of NOx. Processes that seek to destroy NOx after it has been formed are generally called post combustion processes and they are used when techniques for controlling NOx formation are not adequate to meet the emission limit goal.

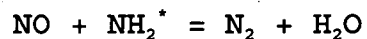
Techniques employed to minimize the formation of NOx are generally accomplished by modifying burners or other components of the overall thermal or chemical process system, and these modifications are typically inexpensive and very cost effective to apply. However, they may not be sufficiently effective to meet regulatory objectives, and post combustion processes must then be applied.

Post combustion processes can effect much lower emission levels than are achievable through the use of techniques that minimize the formation of NOx. Moreover, these processes have been refined over the years to achieve better results and to cost less to

implement, and are widely applied. However, pollution control authorities continue to demand even lower NOx emission levels, and post combustion processes are approaching performance limitations caused by physical and chemical constraints inherent to their methods of operation. The result is a disjoint in the NOx control capability desired by regulatory authorities and the capability which is technically achievable and financially affordable using these processes. This situation produces a need for a different technology that does not have such inherent process constraints because of the manner and method of operation, and therefore can achieve the more aggressive emission limitations desired by the regulatory authorities and needed by society to reduce the effects of air pollution.

Post combustion processes include selective catalytic reduction (SCR), selective non catalytic reduction (SNCR), or a combination of such processes, called the selective hybrid process (SHR). These processes rely on a reagent that is added to the combustion exhaust gases in the presence of a catalyst in the case of SCR, or in a high temperature environment as in the case of SNCR. Practicable reagents include

ammonia and urea. The reagent is injected into the effluent gas stream for reaction with NOx. Urea decomposes to ammonia in the hot gas stream and is therefore an alternative source of ammonia for the SCR, SNCR, and SHR processes and it is often used when the onsite storage of ammonia is deemed a safety risk. In these processes, ammonia dissociates into NH₂* which is a reducing agent to NOx. NH₂* and NOx molecules collide and react to form N₂ and H₂O. The overall chemical reaction is given by:



All three processes are in use, and the selection of the most appropriate process is generally made on the basis of the lowest cost method of meeting the NOx emission goal. The least expensive and also the least effective process is the SNCR process and the most effective NOx reduction technology is currently the SCR process. The SRH process is employed when the SNCR process cannot quite meet the NOx emission and goal and there is a technical need to minimize the use of catalyst material, such as may be caused by space or pressure drop constraints.

The SCR process utilizes a solid catalyst bed located in the effluent stream and the physical

chemistry of gas-solid interface phenomena result in practical performance limitations of the SCR process. One limitation is that some of the ammonia gas will pass through the catalyst bed without becoming absorbed and therefore not dissociate into NH_2^* for reaction with NO_x . This unreacted ammonia is referred to as ammonia slip in the industry, and is in itself a pollutant in effluent streams and hence regulated by pollution control authorities. Furthermore, some of the NO_x can pass through the catalyst bed and not collide with NH_2^* radicals and thereby fail to be controlled by the SCR process, resulting in NO_x emissions.

Another limitation of the SCR process is that the catalyst bed can become fouled or poisoned by contaminants in the effluent gas stream and rendered ineffective. Another limitation is that the catalyst bed can fail to be sealed properly in the reactor vessel causing gas by-passing and the release of unreacted ammonia and NO_x . A further limitation is that the ammonia may not be evenly mixed in the effluent gas stream causing regions of excess ammonia that result in ammonia slip emissions and/or regions of excess NO_x that will not react with NH_2^* completely and pass out the stack uncontrolled. An added limitation is that the

temperature of the effluent gases may not be sufficiently uniform across the catalyst face to cause the catalyst to function optimally, or that the bulk gas temperature is either too low or too high for the catalyst to function optimally. A yet further limitation is that the effluent gas stream can flow through the catalyst bed unevenly, resulting in regions of effluent high velocity and therefore lowers residence times for the reaction.

In addition to the aforementioned functional limitations of the SCR process, the SCR process has other disadvantages to prospective users. These include, but are not limited to, the very large size of the catalyst bed, the cost of the catalyst material, the impact of the pressure drop caused by the catalyst bed, and the magnitude and range of temperature that must be maintained for the chemistry to work properly.

The SCR process requires that the catalyst bed be large enough to achieve a minimum residence time of the reactant gases in the bed in order for the physical chemistry to proceed. This results in large catalyst beds that can often be difficult and expensive to install. The cross sectional area of the bed can be optimized to reduce the bulkiness of the beds, but the

required residence times must be maintained and smaller flow areas must be offset by thicker beds. This causes a non-linear increase in pressure drop and therefore energy cost to maintain flow. Pressure drops through SCR catalyst beds can range from 1 inch water column to more than 5 inches water column. This pressure drop consumes energy to overcome to enable effluent stream flow rate to be maintained.

Catalyst beds associated with the SCR process are also very heavy and this results in the need for significant structural capability of the apparatus and support foundations. The weight also requires heavy lifting equipment during construction. These requirements further add to the installation cost. The materials used to coat the catalyst substrate are rare alloys that are expensive to buy and apply and therefore cause the catalyst material to be undesirably expensive.

The SCR process is also very temperature dependent and it is necessary to make such modifications as necessary in the equipment employed to use the effluent stream so as to make access to the correct temperature window for the SCR reaction. The correct temperature window can range from less than 400°F to as much as 800°F depending on the catalyst material used.

This temperature range is normally found in the middle of a thermal device employed to recover energy from the effluent stream, and access requires the alternation of the heat recovery device at the precise location to enable access to the correct SCR operating temperature. Furthermore, if the heat recovery device is a boiler used for the production of steam, the correct temperature may be within the evaporator tube bundle, whereupon the creation of an installation cavity would be expensive and may cause boiler circulation problems. Therefore, the SCR process is known to have significant physical and chemical shortcomings that cause the SCR process to be understandably expensive to both install and use, and also to have limited NOx reduction performance capability.

Further in regard to the above thermal NOx (NO, N2O, NO2), CO, SOX (SO2, SO3) from mobile and stationary combustion sources are major air pollutants in high-density urban areas. As environmental regulations continue to reduce the emissions in these urban areas, lower-cost methods are needed to create near zero emission combustion sources. The three major methods of post combustion NOx removal are: reducing NOx to N2 with a reactant, oxidizing NOx into nitrogen acids

(HNO₂, HNO₃) with wet scrubbing, and direct absorption on a solid. The method reducing NO_x to N₂ can be further classified as Non-Selective Catalytic Reduction (NSCR), Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR).

Oxidizing NO_x into nitrogen acids with wet/dry scrubbing appears economical only for large stationary combustion sources where there is a fertilizer demand, or where the fuel has high sulfur or ash content, as described in U.S. Patent Nos. 6,605,263 and 6,676,912. U.S. Patent No. 6,605,263 describes how to inject ammonia to convert SO_x into an ammonium salt which is removed with a wet scrubber. U.S. Patent Nos. 6,676,912 and 6,651,638 describe injecting hydrogen peroxide into the gas stream to oxidize NO_x to nitrogen acids and remove the acids with wet scrubbing. U.S. Patent No. 6,523,277 discloses injection of hydrogen peroxide into the exhaust gas and activate it with microwave radiation to oxidize NO_x to nitrogen acids that can be removed with a wet scrubber. U.S. Patent No. 6,743,404 demonstrates how to decompose N₂O contaminant gas into nitrogen (N₂) and oxygen (O₂) gases using a group II metal oxide catalyst (CuO and ZnO on Al₂O₃). U.S. Patent No. 6,612,249 discloses decomposition of NO_x and sequester mercury and

other heavy metals with injection of magnetite in the exhaust gas stream and recovering the product in the ash. U.S. Patent No.6,488,740 describes how to use a wet electrostatic precipitator to remove acid gases (HNO₃) and coal ash. U.S. Patent No.5,843,210 discloses use of an electrostatic spray with scrubber.

Another method of reducing NO_x and Sox in exhaust gases is to adsorb them on a bed. U.S. Patent No.6,506,351 describes how to absorb NO_x and then oxidize the NO_x compounds with ozone to N₂O₅, which can be removed with wet scrubbing during the regeneration cycle. U.S. Patent No.6,503,469 describes how to absorb volatile organic compounds and NO_x in exhaust gas on high-silica adsorbent, and oxide them with ozone. U.S. Patent No.6,066,590 employs a manganese oxide and ruthenium chloride based adsorbent to oxidize NO_x and Sox to acids, and react the acids with an alkali metal to produce a solid salt that remains in the filter.

NSCR methods for mobile combustion sources typically use unburned or oxygenated hydrocarbons, CO, or a reducing agent in the fuel itself to reduce NO_x emissions to N₂. As shown in U.S. Patent Nos. 6,742,326, 5,524,432 and 5,336,476, the fuel/air ratio must be controlled to slip enough reducing agent into

the catalyst to allow the NOx to be reduced to N2. As shown in U.S. Patent No.6,725,643, for a diesel engine, water with an amine compound can be emulsified with the fuel to reduce NOx to N2 in the cylinder. As shown in
5 U.S. Patent No.6,682,709 ammonia or cyanuric acid can be injected down stream of the engine and activated by burning additional fuel to decompose the NOx. As shown in U.S. Patent No.6,612,249, for a stationary combustion source, iron flakes can be used in the combustion
10 chamber to reduce NOx to N2 and absorb mercury vapor. As shown in U.S. Patent No.6,224,839, NOx in exhaust gas can be reduced to nitrogen by reaction with an activated carbon bed impregnated with an alkali metal. The technical challenge is preventing excess oxygen from
15 reacting with the activated carbon to produce carbon monoxide.

SCR methods for stationary lean combustion sources normally employ ammonia or urea to reduce NOX emissions to N2. The solid catalyst surface reduces the
20 activation energy required to reduce NOx with NH3 to produce N2 and H2O by decomposing NH3 to NH*, NH2* radicals or by absorbing NOx on the surface to react with the ammonia. U.S. Patent Nos. 5,744,112 and 5,670,444 describe SCR catalyst compositions of a

mixture of precious metals deposited on a ceramic support structure. The solid catalyst is selective for NOx reduction and not for CO oxidation; therefore CO will remain in the exhaust emission. Since the catalytic reaction requires a slight excess of ammonia ion, NH3, compared to NOx molecules, there is usually a little ammonia slip in the exhaust.

The current state of the art for use of NOx and NH3 slip for high temperature combustion, using a low exhaust gas recirculation and a SCR or SNCR system, is about 4 to 7 ppm for both gases, and for older systems the slip can range from 10 to 25 ppm. U.S. Patent No. 6,287,111 uses staged exhaust gas recirculation to reduce NOx generation by employment of a dual-staged burner system. The current state of the art for NOx generation by means of burners using high exhaust recirculation and low temperature combustion, is about 5-9 ppm. Thus, there is still a need for final polishing of the exhaust to reduce ammonia slip and NOx below 1 ppm to create near zero emission combustion sources.

U.S. Patent No. 6,739,125 discloses use of SCR on a mobile engine while supplying ammonia made from the rich fuel and air mixture.

U.S. Patent No.6,730,125 discloses production of ammonia from the hydrolysis of urea and use of the ammonia in an SCR based NOX treatment process. By injecting ammonia instead of urea, the residence time is reduced in the SCR unit and the NOx conversion is more complete. U.S. Patent No.6,550,250 demonstrates how to make use of an aqueous solution of urea injected into the hot exhaust gases to make ammonia for an SCR. U.S. Patent No. 6,146,605 uses a combined SNCR/SCR process where urea is thermally decomposed into ammonia upstream of the SCR.

Another NSCR method uses an ultraviolet photo-catalyst to remove ammonia and nitrogen monoxide from atmospheric gases. U.S. Patent No.6,566,300 discloses use of titanium oxide on a zeolite carrier as a UV photo-catalyst to decompose ammonia and NO gases. U.S. Patent No.6,562,309 discloses use of a titanium-oxide based, UV photo-catalyst bed to oxidize hydrocarbon fuel vapors. U.S. Patent Nos. 6,468,489 and 6,267,940 discloses injection of a UV photo-catalyst powder (powder SCR catalyst) and ammonia in the exhaust gas, then exposing the exhaust gas mixture to UV light to reduce NOx. The powder catalyst is recovered and recycled. U.S. Patent No.6,153,159 discloses use of a UV

photo-catalyst fluidized bed to reduce NO_x to nitrogen gas while oxidizing unburned hydrocarbons. U.S. Patent NO.6,346,419 uses filtered UV light from a mercury lamp (365 nm bandpass filter) to disassociate NO₂ to NO for chemiluminescence detection.

Another NSCR method uses non-thermal plasma in a catalyst bed to oxidize diesel soot or unburned hydrocarbons to carbon dioxide and reduce NO_x to nitrogen gas, as shown in U.S. Patent Nos. 6,475,350, 6,038,854 and 5,711,147. U.S. Patent Nos. 6,395,238 and 6,139,694 demonstrate how to use a non-thermal plasma and ethanol injection to oxidize NO_x to nitrogen dioxide gas, which is removed with a wet scrubber. U.S. Patent No. 6,365,112 uses a corona discharge to decompose water vapor and oxidize unburned hydrocarbons, NO_x and SO_x so a wet electrostatic precipitator can remove them. Ammonia or urea can be mixed with the water vapor to help reduce NO_x to nitrogen gas. U.S. Patent No.6,345,497 uses an electron beam and U.S. Patent No.6,030,506 uses a hollow cathode discharge to create atomic nitrogen to inject into the exhaust gas stream to reduce NO_x to nitrogen and oxygen gases. The technical challenge for large installations is to mix the atomic nitrogen with the exhaust gas in less than 10

milliseconds. U.S. Patent No.6,176,078 uses a non-thermal plasma to partially oxidize fuel to create a hydrocarbon based reducing agent for an SCR NOx reduction system. An oxidation catalyst is used downstream of the SCR to oxidize any hydrocarbons not used to reduce NOx to nitrogen gas. U.S. Patent No.6,117,403 uses a barrier discharge to oxidize NOx and Sox to acids and then employs a wet scrubber to remove them from the exhaust. U.S. Patent No.6,027,616 uses corona discharge and Helium and an oxygen gas mixture to produce O₂ + ions, which oxidize NOx to nitrogen acids to be removed with a wet scrubber.

None of the above techniques provide the unusually effective methods and results as are now afforded by the present invention.

SUMMARY OF THE INVENTION

It is a major object of the invention to provide apparatus and method that avoids the above limitations, and the subject of this invention addresses the need for a cost effective, readily adaptable and more efficient alternative to the use of conventional post combustion processes to reduce NOx emissions from

effluent gas streams. The subject process herein referred to as the controlled spectrum ultraviolet radiation NOx reduction process, (UVR), is capable of achieving superior NOx reduction performance using the NH3-NOx chemical reaction and with the virtual elimination of excess NH3 emissions. In addition, the UVR process also oxidizes carbon monoxide (CO) gases to harmless CO2.

The present UVR process involves the use of a reagent such as ammonia, urea, or other chemical that yields ammonia gas in the effluent stream, the reagent being injected into the effluent gas stream by means such as by wall nozzles, injector grids or lances for carefully matching the NOx concentration in the effluent stream with the supplied or produced ammonia gas. This injection stage may utilize static mixing devices, multiple injection headers, or other techniques to affect uniform ammonia-NOx distribution.

The present UVR process differs from the SNCR, HRC, or the SCR processes in that means is applied to achieve reaction of the NH3 with the NOx gases after the reagent has been effectively administered to or dispersed in the effluent stream. Promotion of the NH3-NOx interaction involves the use of a controlled

ultraviolet energy source that emits a high intensity energy flux in the form of ultraviolet rays with carefully prescribed wavelengths between 180nm and 280nm and having sufficient intensity to dissociate virtually all NH₃ passing through the ultraviolet beam. The dissociated NH₃ or NH₂^{*} reacts with NO_x to form N₂ and H₂O, the present process more efficiently dissociating the NH₃ gas for promotion of the NH₃-NO_x chemical reaction than the methods employed by the SNCR, SHR, and the SCR processes.

The present UVR process does not require a catalyst bed as is associated with the SCR process, and thereby avoids the aforementioned limitations and disadvantages.

The present UVR process can be applied at any practical temperature consistent with the long term reliability of the UV source and method of application. By avoiding need for high thermal temperatures as are associated with the SNCR process, the UVR process overcomes the efficiency limitations caused by the high temperature reaction chemistry. The process is more efficient for temperatures less than 400 F. Typically, a system and method is provided for photo-catalyzing the oxidation of ammonia to nitrogen gas. UV light between

180 nm and 280 nm is used to convert NH_3 (ammonia) to NH_2^* radical which reacts with NO_x to make N_2 (nitrogen gas) and H_2O (water vapor) at low temperature range (100-35F). UV light between 190 nm and 200 nm is also
5 used to convert H_2O to OH^* radical which reacts with CO to make CO_2 and H_2 .

Although the present UVR process precludes the need for injecting the reagent into high temperature gases, such as used by SNCR or SHR processes, or the
10 need to use a catalyst bed such as in the SHR and the SCR processes, the process can be applied to effluent streams that are already using these processes to enhance their efficiency on such SNCR, HCR, and SCR applications that are experiencing or might soon
15 experience NH_3 - NO_x chemistry limitations as described above, to achieve greater NO_x control and/or to eliminate NH_3 / NO_x emission problems.

In applying the UVR process to existing process systems employing either of the SNCR, SHR, or
20 the SCR processes, the present UVR process is typically installed downstream of such processes and no modifications to the reagent injection system would be mandatory. This invention also contemplates application of the UVR process to effluent gas streams that already

employ post combustion control processes, for
controlling NOx emissions.

In accordance with the above it is an object
of the invention to provide a best mode method for
reducing or substantially eliminating oxides of nitrogen
from a hot effluent gas stream that includes the steps:

a) providing a source of ultraviolet
radiation associated with a duct passing said effluent
stream,

b) adding ammonia to the stream, upstream
of the ultraviolet radiation source,

c) controllably operating said ultraviolet
radiation source to irradiate said stream flowing in the
duct, to effect reduction or substantial elimination of
said oxides of nitrogen by promoting, reaction of
ammonia with said oxides of nitrogen, to produce NO and
H₂O flowing in the stream.

As will be seen, the method typically includes
controlling the rate of ammonia added to said stream to
promote said reduction or substantial elimination of
oxides of nitrogen from the stream the oxide content
subject to variance. Operation of the radiation source
is effected to control the wavelength of said radiation

to dissociate substantially all of the ammonia added into said stream.

Another object includes effecting thorough mixing of ammonia added into said effluent stream, prior to irradiation. The stream may be sampled, upstream of and downstream of the locus of UV radiation, to determine the most efficient rate of ammonia addition to the flowing stream of hot effluent gas.

Another object is to control the temperature of the irradiated effluent to be less than 400°F; and to control the wavelength of radiation to between 180 and 280 nanometers, for most efficient operation, and NOx conversion.

Yet another object is to locate the UV source or sources in the duct, for example in the form of elongated tubular irradiation means clustered in the duct, whereby the effluent stream passes closely adjacent the irradiation means. The tubular means may include multiple tubes located crosswise of the flow in the duct, so that effluent passes efficiently alongside the tubes and in the duct space extending about the tubes. Reflecting means may be provided to enhance efficiency by reflecting emitted radiation back into the gas flow space in the duct.

5 The effluent gas may be generated as by a
combustion process; and the input effluent stream may
contain CO, the radiation controlling step acting to
achieve substantially complete oxidation of the CO to
CO₂.

 These and other objects and advantages of the
invention, as well as the details of an illustrative
embodiment, will be more fully understood from the
following specification and drawings, in which:

DRAWING DESCRIPTION

Fig. 1 is a process flow diagram;

15 Fig. 2 is an enlarged section taken through a
duct, showing an ultraviolet emitting tube cluster;

 Fig. 3 is a section, like Fig. 2, but showing
a modification;

 Fig. 4 is a view like Fig. 3, but showing use
of a reflector; and

20 Fig. 5 is a view like Fig. 2, but showing a
succession of UV emitting tube clusters, in a duct or
ducts.

DETAILED DESCRIPTION

Referring first to Fig. 1, effluent gas, as from a combustion process, flows at 10 and 11 to treating apparatus 12. The gas may originate as in a stack or other outlet 13, from a combustion process. The effluent gas stream may typically contain NO, NO₂, NO₃ (all or some referred to generally as NOX); C, O₂, CO, CO₂, H₂O, as well as unreacted fuel components, such as carbon-hydrogen molecules.

Fresh air may be controllably added at 19 as via a control valve 22 at 20 to the effluent stream, flowing in duct 30. NH₃ and/or urea is controllably added at 23 as via a controllable valve 24, to be distributed as by nozzles 24a in a manifold 24b. An effluent - ammonia gas mixing zone or plenum may be provided in 30 as at 25, upstream of 12.

Apparatus 12 includes a duct section 30a, also seen in Fig. 2, containing an ultraviolet radiation source to irradiate the effluent gas or gases, or mixture, flowing therein between inlet 31 and outlet 32. See arrows 33 showing gas flowing in the treatment zone or spaces 34 outwardly of the UV sources. Those sources are shown in the form of elongated UV bulbs or tubes, as

for example fluorescent tubes 49 extending transversely of the duct, to radiate UV into the spaces between the tubes 49 and also upstream and downstream of the tubes. A static mixer 35 is located upstream of the tubes 49 with transversely spaced flow passes 35a to effect thorough mixing of the gases including NH_3 and NO_x , prior to irradiation. A control for such UV emission is indicated at 37, electrically connected at 38 to the tubes. Best results in terms of NO_x reduction are achieved when the wavelength or wavelengths of UV emission are between 180 and 280 nanometers. Also, best results are achieved when the temperature of the reaction zone 34 is maintained at less than 400°F , and preferably between 100°F and 400°F . For this purpose, a heat exchanger (cooler) may be provided as at 40 in series with the input flow. Output flow at 41 may be sampled as via line 42 and sampler or analyzer 43, whereby the mix of input gases may be varied as by control of O_2 and NH_3 inputs, as at 22 and 24 to achieve maximum reduction of NO_x . See also sampling line 44 connected to the input line at the input side of the apparatus 12, and extending to the analyzer 43 for comparison of NO_x input and NO_x outputs, aiding in such mix control.

Fig. 3 is a view like Fig. 2, but showing clustered UV tubes 46 extending lengthwise in a duct 47, and radiation 48 in flow space 49. Tubes 46 are clustered centrally of the duct.

5 Fig. 4 shows use of a reflector 50, lining the duct 47 inner wall 47a, for reflecting emitted UV back into the treatment zone 49 to enhance efficiency of conversion.

10 Fig. 5 shows use of multiple UV emitters 60, in sections 60a spaced along the interior of duct 59, to repeatedly treat the gases with ultraviolet radiation, to enhance completeness of NOX elimination. The emitters extend transversely as in Fig. 2. Note mixing zones or plenums 62 between the emitter sections in
15 which treated gas may mix to more uniformly disperse remanent concentrations of unreacted NOX, prior to subsequent UV treatments. Controls for such emitters 60 (such as in Figs. 1-4) are indicated at 66 and 67, whereby intensity and wavelength of the radiation from
20 the emitters can be independently controlled, for optimum operation.

The diameter of duct 59 can be locally enlarged, outwardly of any of emitters 60, to slow the

flow adjacent those emitters, to increase UV treatment time.

In Figs. 1 and 2, the duct 30 extends in a Z-direction; the tubes 49 extend in parallel relation in an X direction; and the tubes 49 are spaced apart in a Y direction, whereas X, Y and Z are coordinates in a rectangular coordinate system. In Figs. 3-5 the tubes extend in the Z direction, and are spaced apart in X and Y directions.

WE CLAIM:

1. A method for reducing or substantially eliminating oxides of nitrogen from a hot effluent gas stream, that includes

a) providing a source of ultraviolet radiation associated with a duct passing said effluent stream,

b) adding ammonia to said stream, upstream of said ultraviolet radiation source,

c) controllably operating said ultraviolet radiation source to irradiate said stream flowing in the duct, to effect reduction or substantial elimination of said oxides of nitrogen by promoting reaction of ammonia with said oxides of nitrogen, within the temperature range 100-400°F, to produce N₂ and H₂O flowing in the stream.

2. The method of claim 1 including controlling the rate of ammonia added to said stream to promote said reduction or substantial elimination of oxides of nitrogen from the stream.

3. The method of claim 2 including sampling said stream upstream and downstream of the locus of radiation, to determine most efficient rate of ammonia addition to said stream, for conversion of oxides of nitrogen.

4. The method of claim 1 including effecting thorough mixing of ammonia added into said effluent stream.

5. The method of claim 1 wherein said operation of the radiation source is effected to control the wavelength of said radiation to dissociate substantially all of the ammonia added into said stream.

6. The method of claim 5 wherein the wavelength or wavelengths of radiation is controlled to between 180 and 280 nanometers.

7. The method of claim 1 wherein the temperature of the irradiated effluent is controlled to be less than 400°F.

8. The method of claim 1 including locating said source in the duct.

9. The method of claim 8 wherein the source is provided in the form of elongated, spaced apart irradiation means extending in the duct, and transversely thereof whereby the effluent stream passes over said spaced apart means.

10. The method of claim 8 wherein the tubular means includes multiple tubes located generally centrally in the duct.

11. The method of claim 10 includes providing reflection means associated with the duct, outwardly of the source, and operating to reflect ultraviolet radiation back into the flowing stream.

12. The method of claim 1 including providing and operating a combustion process for producing said oxides of nitrogen.

13. The method of claim 1 wherein said effluent stream contains CO, and said controlling step acts to achieve substantially complete oxidation of CO to CO₂, in the duct.

14. The method of claim 1 including operating one of the following processes to produce said effluent gas stream, upstream of said source of ultraviolet radiation:

- i) an SNCR process
- ii) an SHR process
- iii) an SCR process

15. The method of claim 1 including providing at least one additional source of UV emission, downstream in the duct, and a gas mixing plenum or plenums between said sources.

16. The method of claim 15 including the step of independently controlling intensity and wavelength of ultraviolet radiation from said sources.

17. Apparatus for reducing or substantially eliminating oxides of nitrogen from a hot effluent gas stream, that comprises:

- a) a duct and a source of ultraviolet radiation associated with said duct passing said effluent stream,
- b) means for adding ammonia to said stream, upstream of said ultraviolet radiation source, and
- c) means for controllably operating said ultraviolet radiation source to irradiate said stream flowing in the duct, to effect reduction or substantial elimination of said oxides of nitrogen by promoting, reaction of ammonia with said oxides of nitrogen, to produce N_2 and H_2O flowing in the stream.

18. The apparatus of claim 1 wherein said source of ultraviolet radiation comprises UV emitting tubes extending in generally clustered relation.

19. The apparatus of claim 18 wherein said tubes extend in parallel relation in an X-direction; the tubes being spaced apart in a Y-direction; and the duct extending in a Z-direction, where said directions are the X, Y and Z directions in a rectangular co-ordinate system.

ABSTRACT OF THE DISCLOSURE

5 A method for reducing or substantially
eliminating oxides of nitrogen from a hot effluent gas
stream, that includes providing a source of ultraviolet
radiation associated with a duct passing the effluent
stream, adding ammonia to the stream, upstream
of the ultraviolet radiation source, controllably
operating the ultraviolet radiation source to irradiate
the stream flowing in the duct, to effect reduction or
10 substantial elimination of the oxides of nitrogen by
promotion, reaction of ammonia with the oxides of
nitrogen, to produce NO and H₂O flowing in the stream.

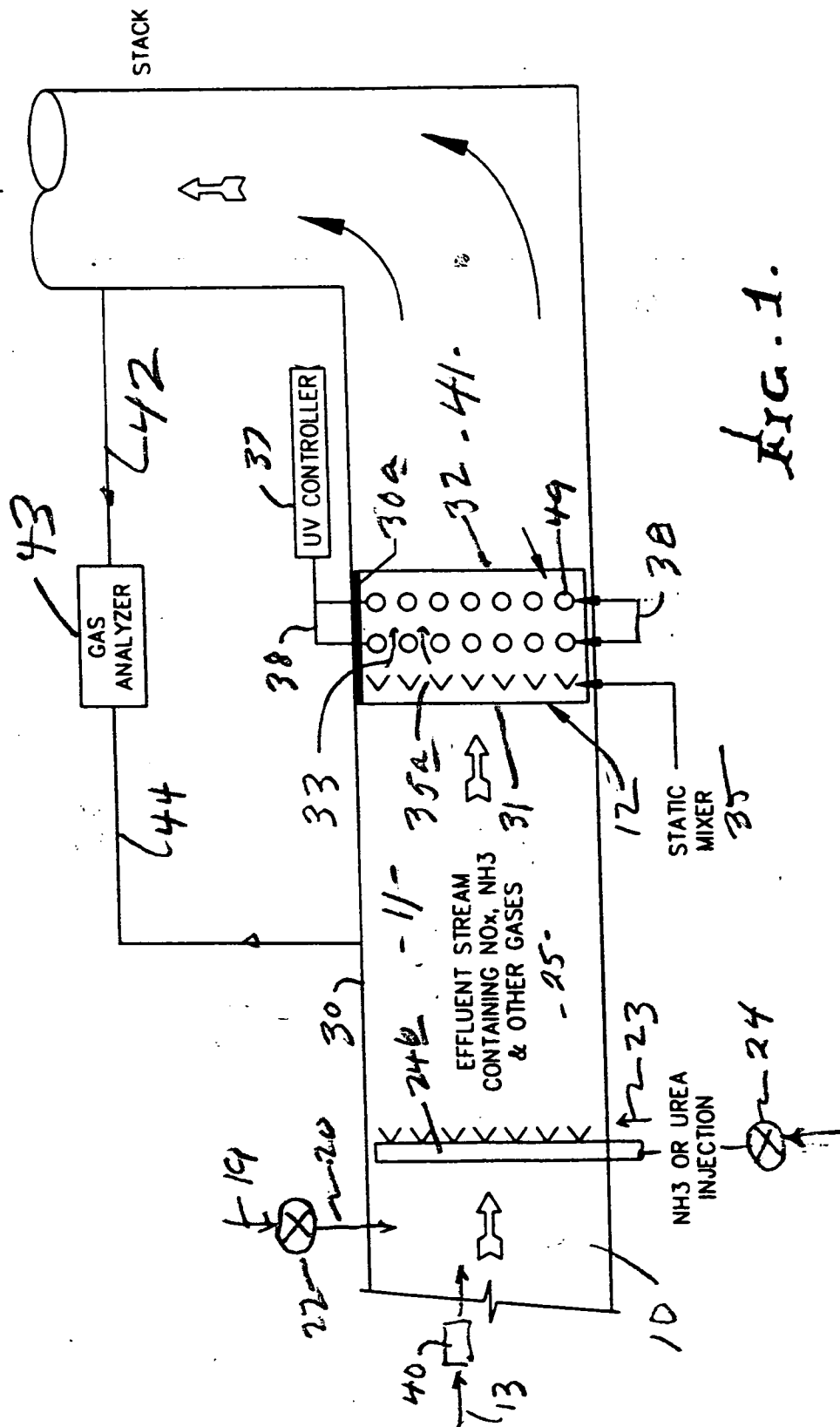


FIG. 1.

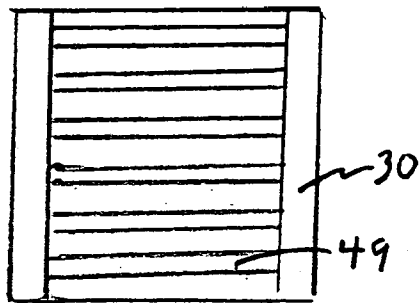


FIG. 2.

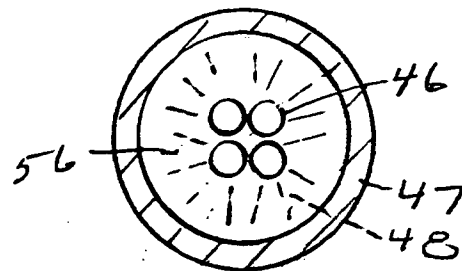


FIG. 3.

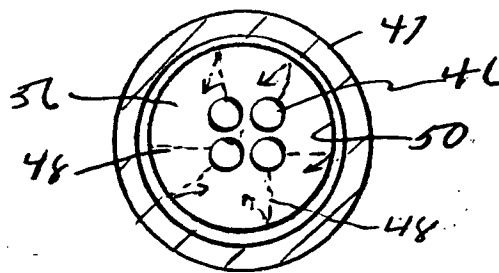


FIG. 4.

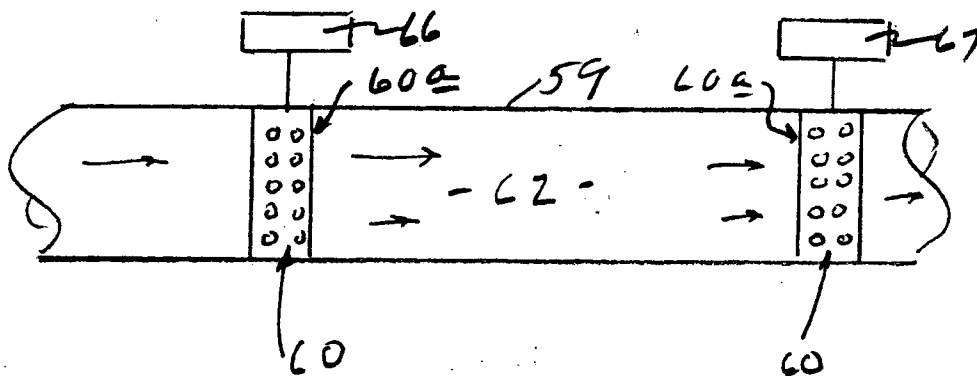


FIG. 5.